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A PROPOSED INTERPRETATION OF THE DESTABILIZING EFFECT OF HYDROXYL GROUPS ON NITROAROMATIC MOLECULES

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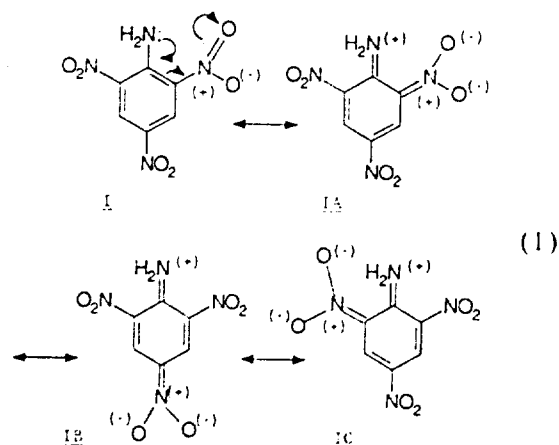
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Whereas an amino group stabilizes nitroaromatic molecules toward shock and impact, presumably through a resonance interaction that strengthens the C-NO₂ bonds, hydroxyl substituents have a sensitizing effect despite having resonance capabilities. This may reflect the formation, by hydroxyaromatics, of the unstable nitronic acid tautomer. A computational analysis (SCF, 3-21G) of the *o*-nitrophenol system, used as a model, shows that transfer of the phenolic proton to the nitro group produces an equilibrium nitronic acid structure, with a calculated energy 15.4 kcal/mol above *o*-nitrophenol. Such proton transfer might result from vibrational excitation of the O-H bond produced by shock or impact. No analogous equilibrium structure is found for a possible nitronic acid tautomer of *o*-nitroaniline.

One of the important objectives of current research in the area of high-energy molecules is to learn more about the factors that determine their sensitivities toward shock and impact. A better understanding of these factors could lead to the design and synthesis of chemical systems that combine high performance with improved stability.

With regard to nitroaromatic molecules, there has been some progress in relating measured sensitivities to structural and/or electronic properties [1-5]. Certain empirical observations have also been made. It has been found, for example, that the amino group has a stabilizing influence on nitroaromatics [1]; 1,3-diamino-2,4,6-trinitrobenzene and 1,3,5-triamino-2,4,6-trinitrobenzene are among the least sensitive members of this class (table 1).

One interpretation of this is that amino substituents, being strong resonance donors, [6] strengthen the C-NO₂ bonds, as shown below for 2,4,6-trinitroaniline, I:



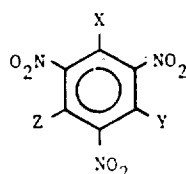
The introduction of additional -NH₂ groups would be expected to enhance the effects shown in structures IA-IC. Since there is evidence that the rupture of C-NO₂ bonds is a key step in the decomposition of nitroaromatics [7-9] the strengthening of these bonds that is depicted in eq. (1), if it actually occurs, could certainly account for the observed decrease in sensitivity.

Data are available to support the argument that amino substituents do indeed produce a strengthening of the C-NO₂ bonds in nitroaromatic systems. Table 1 lists the crystallographically determined C-NO₂ and N-O bond lengths for a group of nitroaromatics. Taking 1,3,5-trinitrobenzene as a reference point, it can be seen that the introduction of amino groups produces, overall, a progressive shortening of the C-NO₂ distances and a lengthening of the N-O. Both of these trends are exactly the consequences predicted by eq. (1) of the delocalization of amino lone pairs into the aromatic ring.

It can reasonably be proposed, therefore, that amino groups diminish the sensitivities of nitroar-

omatics by strengthening the C-NO₂ bonds. It would appear that the same sort of arguments could be applied to hydroxynitro-aromatics, such as picric acid (2,4,6-trinitrophenol, II); the hydroxyl group is also a strong resonance donor [6], and structures analogous to IA-IC can be drawn. In reality, however, picric acid has been found to be quite sensitive, and the same is true of the di- and tri-hydroxy systems (table 1). On the other hand, methoxy (-OCH₃) nitroaromatics, for which resonance structures of the types IA-IC can also be written, show the same sensitivity trend as do amino derivatives [2]. Our primary objective in this work has been to arrive at a reasonable interpretation of the observed sensitizing effect of the hydroxyl group.

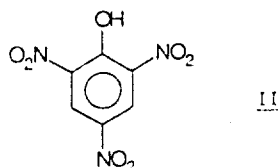
Table 1
Experimentally determined properties of some trinitroaromatic molecules



Molecule	Sensitivity ^{a)} (cm)	C-NO ₂ distances (Å)	N-O distances (Å)
X=Y=Z=OH ^{b)}	27	1.436 1.436 1.466	1.228, 1.240 1.228, 1.240 1.221, 1.221
X=Y=OH, Z=H ^{b)}	43	1.456 1.456 1.468	1.217, 1.235 1.217, 1.235 1.217, 1.217
X=OH, Y=Z=H ^{c)}	87	1.454 1.456 1.478	1.215, 1.218 1.201, 1.227 1.182, 1.202
X=Y=Z=H ^{d)}	100	1.473 1.477 1.495	1.195, 1.208 1.179, 1.219 1.179, 1.214
X=NH ₂ , Y=Z=H ^{e)}	177	1.463 1.469 1.475	1.202, 1.230 1.224, 1.224 1.215, 1.220
X=Y=NH ₂ , Z=H ^{f)}	320	1.415 1.432 1.514	1.241, 1.262 1.223, 1.260 1.177, 1.236
X=Y=Z=NH ₂ ^{g)}	> 320	1.417 1.417 1.422	1.236, 1.242 1.239, 1.246 1.244, 1.252

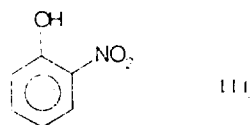
^{a)} The sensitivity data refer to impact, and represent the heights from which a given weight must be dropped on the compound to produce detonation. Thus, the smaller the value given, the more sensitive is the compound toward impact. The data are taken from ref. [2].

^{b)} Ref. [10]. ^{c)} Ref. [11]. ^{d)} Ref. [11]. ^{e)} Ref. [13]. ^{f)} Ref. [14]. ^{g)} Ref. [15].

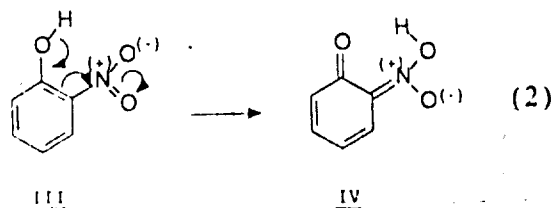


The combined electron-withdrawing power of the three nitro groups in picric acid makes the hydroxyl hydrogen quite positive in nature. For example, whereas phenol is very weakly acidic, with $pK_a = 9.9$, picric acid is a relatively strong acid; its pK_a of 0.38 is comparable to that of trichloroacetic acid (0.70) [16]. In the solid phase, the crystal structure of picric acid indicates significant hydrogen bonding between the hydroxyl and an ortho nitro group [11]. The O...O separation is 2.55 Å, which is near the shorter end of the range that has been identified as typical of O-H...O hydrogen bonds (2.50–2.80 Å) [17].

Since crystallographic measurements cannot locate hydrogens with precision, we have carried out a computational analysis of this intramolecular hydrogen bonding, taking *o*-nitrophenol (III) as a model so that the calculations could be performed at a reasonably high level. An optimized geometry was determined for III at the SCF level with the 3-21G basis set using the GAUSSIAN 86 program [18]; the 3-21G basis has been shown to be effective for this purpose [19].



Our calculated structure for III is shown in table 2. The separation of the two oxygens involved in the hydrogen bonding is 2.55 Å (the same as was found crystallographically for picric acid). The H...O distance is 1.75 Å. The labile nature of this hydrogen and its proximity to the nitro oxygen suggested that it would be worth investigating whether there is any significant probability of hydrogen migration to the nitro oxygen. The proposed process is represented by

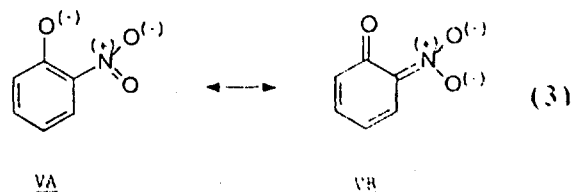


IV is a nitronic acid; these are known to be reactive, unstable systems [20]. Thus, if a process analogous to eq. (2) were to occur for picric acid (II), this would represent a decomposition mechanism that could account for its instability. A similar reasoning would apply to the dihydroxy and trihydroxy compounds. It is relevant to point out that there is experimental evidence linking the sensitization and decomposition of nitroalkanes to the presence of nitronate anions [21,22].

In order to assess the likelihood of the proton transfer described by eq. (2), we carried out a 3-21G geometry optimization of the nitronic acid IV. An energy minimum was indeed found; the equilibrium structure is given in table 2. At the 3-21G level, IV is 15.4 kcal/mol higher in energy than III. The C-N distance in IV is 0.08 Å shorter than in III, consistent with a higher degree of double bond character, while the N-OH length has increased to a value typical of an N-O single bond [23]. The C-C distances in the aromatic ring now show pronounced diene character.

The structures in table 2 show that the proton in *o*-nitrophenol (III) need move only a relatively short distance in the direction of the nitro oxygen for the system to reach a local energy minimum corresponding to the nitronic acid IV. Such motion could be, for example, the result of excitation to a higher O-H vibrational level.

An interesting perspective can be obtained by looking at the anions of III and IV. Eq. (2) can be viewed as the transfer of a proton from the *o*-nitrophenolate anion VA to the nitronate anion VB. In the absence of the proton, however, there is no structural difference between VA and VB, and they are really just two resonance contributors to one anionic system, V.



We have computed the 3-21G optimized geometry of V and used this structure, shown in table 2, to ob-

tain its electrostatic potential. This is the potential $V(r)$ that is created at any point r in the space around a molecule by its nuclei and electrons; it is a real

physical property that is given rigorously by

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr' \quad (4)$$

Table 2

Calculated structures for *o*-nitrophenol (III), its nitronic acid tautomer (IV), the *o*-nitrophenolate (or nitronate) anion (V), and *o*-nitroaniline (VI). The bond lengths are given in Å, the bond angles in deg

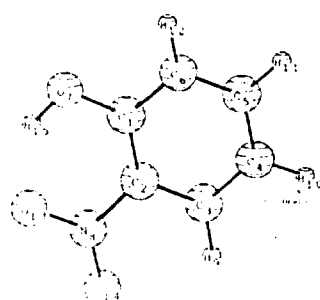
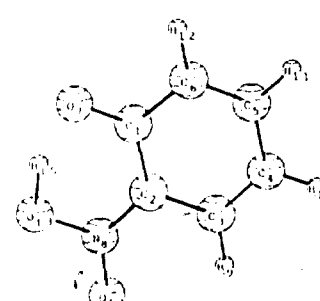
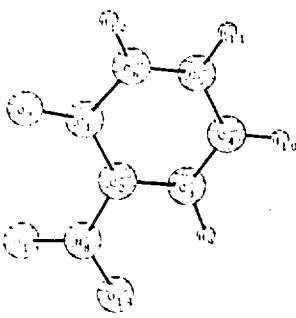
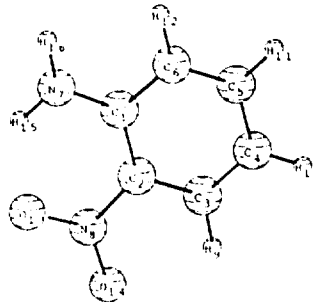
		Bond length		Bond angle	
<i>o</i> -nitrophenol, III		C1-C2	1.392	C2-C1-C6	117.7
		C1-C6	1.394	C2-C1-O7	124.9
		C1-O7	1.344	C1-C2-C3	121.2
		C2-C3	1.393	C1-C2-N8	120.9
		C2-N8	1.431	C6-C1-O7	117.4
		C3-C4	1.366	C1-C6-C5	120.9
		C3-H9	1.067	C1-C6-H12	117.1
		C4-C5	1.398	C1-O7-H15	111.2
		C4-H10	1.070	C3-C2-N8	117.9
		C5-C6	1.369	C2-C3-C4	120.3
		C5-H11	1.071	C2-C3-H9	118.0
		C6-H12	1.069	C2-N8-O13	118.2
		O7-H15	0.976	C2-N8-O14	118.8
		N8-O13	1.272	C4-C3-H9	121.7
		N8-O14	1.233	C3-C4-C5	119.0
nitronic acid tautomer of <i>o</i> -nitrophenol, IV		C1-C2	1.441	C2-C1-C6	115.5
		C1-C6	1.437	C2-C1-O7	121.8
		C1-O7	1.261	C1-C2-C3	121.6
		C2-C3	1.426	C1-C2-N8	119.3
		C2-N8	1.347	C6-C1-O7	122.7
		C3-C4	1.340	C1-C6-C5	121.4
		C3-H9	1.068	C1-C6-H12	116.1
		C4-C5	1.436	C3-C2-N8	119.2
		C4-H10	1.069	C2-C3-C4	120.0
		C5-C6	1.343	C2-C3-H9	118.0
		C5-H11	1.072	C2-N8-O13	118.9
		C6-H12	1.069	C2-N8-O14	124.9
		N8-O13	1.383	C4-C3-H9	122.0
		N8-O14	1.234	C3-C4-C5	119.5
		O13-H15	1.050	C3-C4-H10	120.9
				C5-C4-H10	119.6
				C4-C5-C6	122.0
				C4-C5-H11	118.5
				C6-C5-H11	119.5
				C5-C6-H12	122.5
				O13-N8-O14	116.2
				N8-O13-H15	105.0

Table 2 (continued)

		Bond length		Bond angle
o-nitrophenolate (or nitronate) anion, V 	C1-C2	1.446	C2-C1-C6	112.3
	C1-C6	1.465	C2-C1-O7	127.8
	C1-O7	1.240	C1-C2-C3	122.0
	C2-C3	1.407	C1-C2-N8	121.9
	C2-N8	1.397	C6-C1-O7	119.9
	C3-C4	1.354	C1-C6-C5	124.2
	C3-H9	1.067	C1-C6-H12	114.6
	C4-C5	1.423	C3-C2-N8	116.1
	C4-H10	1.072	C2-C3-C4	122.5
	C5-C6	1.344	C2-C3-H9	116.0
	C5-H11	1.076	C2-N8-O13	120.7
	C6-H12	1.072	C2-N8-O14	118.6
	N8-O13	1.253	C4-C3-H9	121.5
	N8-O14	1.291	C3-C4-C5	117.9
o-nitroaniline, VI 	C1-C2	1.404	C2-C1-C6	116.1
	C1-C6	1.413	C2-C1-N7	124.3
	C1-N7	1.346	C1-C2-C3	121.2
	C2-C3	1.397	C1-C2-N8	122.0
	C2-N8	1.428	C6-C1-N7	119.5
	C3-C4	1.362	C1-C6-C5	121.9
	C3-H9	1.067	C1-C6-H12	117.9
	C4-C5	1.400	C1-N7-H15	118.9
	C4-H10	1.069	C1-N7-H16	120.2
	C5-C6	1.363	C3-C2-N8	116.8
	C5-H11	1.072	C2-C3-C4	121.3
	C6-H12	1.071	C2-C3-H9	117.2
	N7-H15	0.997	C2-N8-O13	119.3
	N7-H16	0.995	C2-N8-O14	118.2
	N8-O13	1.262	C4-C3-H9	121.5
	N8-O14	1.245	C3-C4-C5	118.4
			C3-C4-H10	120.8
			C5-C4-H10	120.8
			C4-C5-C6	121.1
			C4-C5-H11	119.7
			C6-C5-H11	119.2
			C5-C6-H12	120.2
			H15-N7-H16	120.8
			O13-N8-O14	122.5

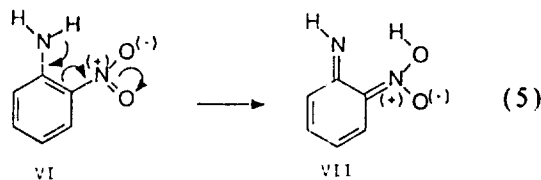
Z_A is the charge on nucleus A , located at R_A and $\rho(r)$ is the electronic density, which we obtain from the molecular wavefunction. $V(r)$ was computed at the 6-31G* level; it was considered necessary to use a

large basis set, including polarization functions, to take account of the diffuse electronic distribution associated with an anion.

The electrostatic potential in the molecular plane

of V is plotted in fig. 1. There are strong and extensive negative regions surrounding the system, as is to be expected for an anion. However the single most negative value of the potential is at a point that is essentially equidistant from the two oxygens involved in the hydrogen bonding. This site, not associated specifically with either oxygen, is where a proton approaching the anion would initially be attracted. A short movement toward either of the oxygens would then produce one of the two equilibrium structures that we have found, III or IV.

Since our motivation for this work was to try to understand the contrasting sensitivities of hydroxy and amino derivatives of nitroaromatics, it is necessary to investigate whether the proton transfer shown in



which is analogous to eq. (3), could occur in *o*-ni-

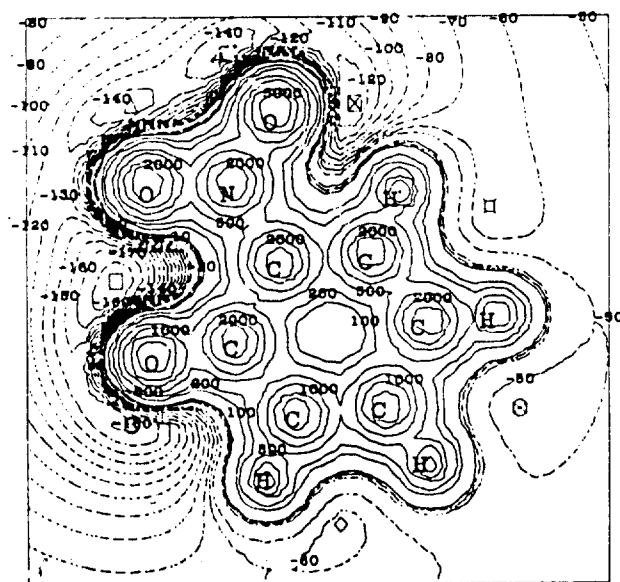
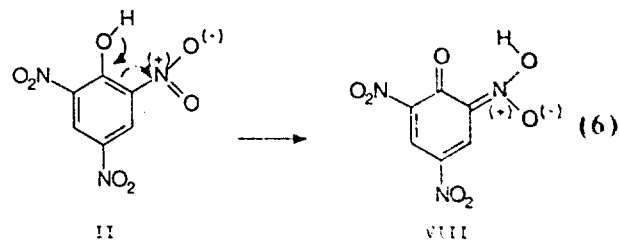


Fig. 1. Calculated electrostatic potential of the anion V, in kcal/mol, in the molecular plane. Dashed contours correspond to negative values. The locations of the most negative potentials are indicated, and the corresponding magnitudes are given at the side of the plot.

troaniline, VI, which might also be expected to show intramolecular hydrogen bonding. Indeed our 3-21G geometry optimization of VI shows the relevant N...O separation to be 2.61 Å with H...O, 1.89 Å (table 2); these are certainly indicative of a hydrogen bonding interaction. However despite exhaustive efforts to obtain an optimized structure for the nitronic acid VII, we were unable to find an energy minimum corresponding to this system. There appears to be no tendency for the proton transfer represented by eq. (5) to occur.

On the basis of the results that have been presented in this paper, we suggest that the observed high sensitivity of picric acid toward shock and impact (table 1) may be due to some significant fraction of its molecules being in the form of an unstable nitronic acid (VIII), produced through the process represented by



The proton transfer shown in eq. (6) could result, for example, from a vibrational excitation of the O-H bond brought about by the energy input associated with picric acid being subjected to shock or impact.

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